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Thermal and electric field stability of square-net domain patterns in barium titanate

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We use polarized light microscopy *in situ* with an externally applied electric field to induce square-net birefringence patterns in top-seeded single crystals of barium titanate above the Curie temperature (T_C). The patterns occur under a wide range of electric field magnitudes larger than ~ 0.2 kV/mm and at temperatures up to 6°C above T_C . We mapped this behavior on a pseudophase diagram showing the region in electric field and temperature space where this domain configuration is stable. We observed the electric field induced transformation into the periodically ordered structure from both the cubic structure above T_C and the tetragonal structure below T_C . Synchrotron x-ray reciprocal space maps indicate the presence of ferroelastic domains perpendicular to the electric field direction at a range of electric field magnitudes similar to those required to induce the periodic domain ordering we observe using polarized light microscopy. Combined with a simple model of the optical retardation, we show that the periodic domain ordering responsible for the square-net birefringence occurs only at the surfaces of the crystals and that these domain structures are unexpectedly invariant with respect to the electric field that induces them.

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I. INTRODUCTION

Barium titanate may well be the most archetypal ferroelectric [1–5]. But despite this, one particularly long-standing mystery is the self-organization of domains that gives rise to square-net birefringence patterns under certain conditions close to the Curie temperature (T_C) [6–9]. The origin of these patterns are debated, but for 70 years have only been observed in certain flux-grown single crystals during the para- to ferroelectric phase transition just below T_C . These square-net patterns are well recognized due to their spectacular nature when viewed with polarized light microscopy. However, it is not completely understood why these patterns occur under such a narrow range of conditions, or even what the full extent of these conditions may be.

Square-net birefringence patterns were first observed in BaTiO₃ in 1949 by Forsbergh [6], who studied the thermal stability of the patterns and proposed a possible explanation for the birefringence contrast in terms of a structure of intersecting wedged domains. After many years of dormancy on the topic, Schilling *et al.* [9] proposed an alternative domain structure that explained this birefringence, along with a corresponding phenomenological theory for the self-ordering of this domain structure below the T_C . Finally, Walker *et al.* [8] used white beam x-ray topography to measure the surface strain due to the formation of these self-organized domains, mapping the distribution of elastic and spontaneous strain as a function of temperature. Crucially, these studies investigated the occurrence of the square-net pattern in the absence of an external electrical field. As such, the proposed domain structures that give rise to the square-net patterns require electric neutrality [9]. Furthermore, it was also concluded

that the square-net pattern is restricted to specific flux-grown crystals and was not possible in crystals grown via top-seeded approaches [8]. With the understanding that top-seeded crystals tend to be purer than the flux-grown equivalents, these observations point to the conclusion that the phenomena is likely defect driven [7].

By heating a top-seeded-grown single crystal of BaTiO₃ to near the T_C and simultaneously applying an electric field, we observed a square-net birefringence pattern similar to those reported for flux-grown crystals. The pattern appears to be stable in a large temperature range around T_C and at electric field magnitudes above a critical value. By acquiring *in situ* polarized light microscopy videos of the transition from cubic or tetragonal phases and digitally identifying the square-net pattern at varying fields and temperatures, we track the onset of the square-net pattern and construct a pseudophase diagram to describe its region of stability [10–12]. A representative image of the patterns we observe can be seen in Fig. 1. In this paper we show that the square-net effect is stable in a well defined electric field—temperature regime close to the para- to ferroelectric phase transition.

Figure 1 shows an example of the electric-field induced square-net birefringence pattern. When the electric field is first increased, tetragonal domains polarized perpendicular to the field grows out from the electrode (from cold to hot). Remnants of this domain type can be seen close to the electrode on the left side of Fig. 1, marked (i), where the sample is at the lowest temperatures. At a critical field strength, depending on the sample temperature, the growing tetragonal phase start to display the square-net domain ordering, as seen centrally in Fig. 1, marked (ii). Due to the temperature gradient in the sample, this critical electric field magnitude varies across the sample. At measured temperatures above 145°C , the square-net pattern is not observed, and increasing the electric field

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FIG. 1. (a) BaTiO_3 observed at 0.4 kV/mm and at a sample holder temperature of 142.7 °C. (i) Close to the electrode the sample is cool and domains are polarized parallel to the surface. (ii) Square-net pattern is observed in an area between the electrode and sample holder. (iii) Domains polarized parallel to the electric field are observed at high temperature near the boundary to the sample holder.

magnitude will result in a transformation into the tetragonal phase, whose domains are polarized parallel to the field. This state can be seen in the right part of Fig. 1, marked (iii). The sample temperature is highest in this region due to being close to the copper edge of the sample holder. At this temperature (142.7 °C), the transformation from cubic to tetragonal is only visible for a short period where the tetragonal phase front appears as surface domains polarized perpendicularly to the electric field, before quickly reorienting parallel to the electric field direction and disappearing from view.

II. SAMPLE PREPARATION

The experiments were carried out on a commercially grown (Crystal GmbH, Germany) BaTiO_3 single crystal, grown via the top-seeded method and polished to $5 \times 5 \times 0.15 \text{ mm}^3$. A custom-designed apparatus [13] was used to precisely control the temperature of the crystal and its applied electric field during the experiments. Optically transparent electrodes were applied to the $5 \times 5 \text{ mm}^2$ faces by coating them with a thin layer ($\sim 100 \text{ nm}$) of indium tin oxide (ITO) using magnetron sputtering at 100 °C for 30 min. The two ITO electrodes reduced the optical transmission of the sample to 80%–90% for visible light, while giving an electrical resistivity on the order of $\sim 10^{-4} \Omega/\text{cm}$ [14,15]. While the bottom face of the sample was in electrical and thermal contact with the electrically grounded sample holder, an electrode was connected to the top side using a thin copper wire and silver paste.

This silver paste at the electrode-wire junction facilitated heat loss through the wire and resulted in a temperature gradient over the sample, as observed by the three regions indicated in Fig. 1. This temperature gradient is responsible for the (potentially) erroneous observation of different phase transition temperatures across the sample.

FIG. 2. Method for tracking square-net patterns and calibrating the temperature scale. (1) An image from the video is loaded. For each image the sample holder temperature and applied electric field has been recorded. (2) Squares on the loaded image are detected. (3) Using the temperature map constructed from the phase transition temperature a temperature is assigned to each detected square. (4) Temperature and electric field values for the square-net pattern are recorded on the phase diagram.

We measured the magnitude and spatial distribution of temperature gradients across the image field-of-view by recording the zero-field phase transition from tetragonal to cubic. By assuming that T_C (141 °C measured at the thermocouple at the edge of the sample) [16] is invariant across the sample, we created a spatial map of the difference between the thermocouple temperature and the local phase transition temperature for each pixel in the image. This calibration map (see Fig. 2) then enabled reliable and precise determination of the temperature and electric field strength in each pixel of the polarized light microscopy images. These measurements show a maximum temperature difference of up to 6 K from the electrode to the sample holder edge.

III. IN SITU POLARIZED LIGHT MICROSCOPY

In order to map the transition between the paraelectric phase, the ferroelectric phase, and the square-net pattern within that ferroelectric phase, we conducted *in situ* polarized light microscopy experiments at varying temperatures and electric field strengths. Our procedure involved first heating the sample above the T_C (150 °C at the holder), where the transition into the cubic state could be seen as complete darkness in the microscope due to the loss of birefringence. Then, after allowing the system to stabilize at a constant temperature for 2–5 min, the sample was cooled to the desired temperature, after which the electric field was continuously increased from 0–0.8 kV/mm at 6.67 V/(mm s). This procedure was repeated for indicated temperatures ranging from 142 to 149 °C in steps of 1 °C. For reference, a real-time video of the measurements is provided in the Supplemental Material [17].

An Olympus CX31-P microscope with a 4× objective lens and a Olympus SC50 digital camera was used for the polarized light microscopy. All experiments were carried out under crossed polarizers with the primary axis of the sample at 45° angle to the polarization. As such, the intensity transmitted through the sample can be written as

$$I = I_0 \sin^2 \frac{\pi d \Delta n}{\lambda}, \quad (1)$$

where I_0 is the incident intensity, d is the sample thickness, Δn is the birefringence, and λ is the light wavelength in the sample. From this we can expect both the cubic phase and tetragonal domains whose spontaneous polarization is oriented parallel to the incident light to be completely dark, since $\Delta n = 0$. Conversely, tetragonal domains whose spontaneous polarization is perpendicular to the incident light should be visible in the microscopy images as an increased intensity relative to the background. However, we note that, in our observations, electric field-aligned tetragonal domains induced by weak electric fields do not result in complete darkness as expected.

The videos resulting from the series of *in situ* polarized light microscopy experiments at varying temperatures and electric-field magnitudes were then used to track the onset of the square-net pattern, and thus the critical temperature and electric field magnitudes (see Fig. 2). After acquiring the videos of the transformation, the analysis process involved first grayscaling and thresholding the color images into binary representations according to their total intensity. The regions in the binary images were then sorted by their area and eccentricity such that only regions associated with the square-net patterns are considered. By correlating the geometrical properties of the binarized intensity regions to the temperature and applied electric field, a pseudophase diagram detailing the stability of these phases could be constructed (Fig. 3). We note that the temperatures reported in the phase diagram are corrected using the temperature calibration map in the aforementioned manner.

The resulting temperature-electric field pseudophase diagram is shown in Fig. 3, and describes the transformation into and out of the square-net pattern in relation to the more conventionally expected cubic and tetragonal phases, in the temperature and electric field ranges of 138–145 °C and 0.2 kV/mm and above. We note that due to hysteresis the zero field phase transition from cubic to tetragonal is a few degrees below the T_C (141 °C) mentioned above. Though we observe the pattern become less pronounced at high field strengths, we were not able to identify an upper electric field limit due to the high-field capabilities of the sample holding apparatus. We note that some degree of hysteresis is observed when lowering the field as the square-net pattern persists in a range of electric fields, but disappears just before the field is completely removed.

We also mention that crack growth was observed at multiple positions in the sample during the electric field induced phase transition. We assume the cracking occurs due to a combination of the thermal stresses induced by the thermal gradient and the heterogeneous stresses from the spontaneously strained domains that form upon the phase transition. If we assume the domains comprising the square-net pattern

FIG. 3. Pseudophase diagram for the field induced phase transition. Black points marked the observed transitions between “phases.” Periodic domain ordering is observed between the cubic to tetragonal phase transition at sample holder temperatures from 138 to 145 °C. Below this temperature region the sample remains in the tetragonal phase which at high fields align the polarization with the field direction. Above 145 °C the cubic state transits into a tetragonal domains polarized along the electric field direction for high electric field magnitudes.

are surface structures (as concluded by Ref. [8]), they result in a spherical bending of the sample. However, due to the sample being clamped down at the edges, this bending will give rise to tensile stresses on the opposite side to the square-net pattern, which in turn promotes crack initiation and growth. Electrical resistance measurements of the sample surface after the crack growth indicates that the conducting ITO film was not completely broken, and that the field distribution on the sample should be approximately uniform across the cracks.

At this point we note that these observations of electric-field induced square-net patterns and subsequent crack growth were repeated on a second, separate BaTiO₃ sample.

IV. *IN SITU* SYNCHROTRON X-RAY RECIPROCAL SPACE MAPPING

To provide further insight into the structural changes occurring during the transformation to and from the square-net pattern, we repeated the experiment while carrying out *in situ* synchrotron x-ray single crystal diffraction. The experiment was carried out at beamline ID06 at the European Synchrotron (ESRF) at an x-ray energy of 17 keV ($\Delta E/E = 10^{-4}$). Diffraction intensity maps were measured on a high-resolution CCD detector located approximately 5 m from the sample, resulting in a reciprocal space resolution of approximately $10^{-5} \text{ \AA}^{-1}$. The sample environment was heated to 139.6 °C; approximately 1° above the measured transition temperature, and rocking scans through the [2 0 0] Bragg reflection were then carried out at increasing electric field magnitudes 0 to 0.8 kV/mm to investigate the changes to the average crystal structure. By tracking the intensity distribution in reciprocal space as a function of electric field strength,

FIG. 4. Results from reciprocal space maps (RSMs) taken at varying electric fields just above T_C . Above: d spacing of the present $[1\ 0\ 0]$ planes for field strengths between 0 and 0.8 kV/mm. Below: Amount of the sample in the respective phases.

we clearly identify the electric field induced transformation from the cubic to the tetragonal phase, as well as the lattice strains they manifest Fig. 4(a). Close to the phase transition at 0.3 kV/mm, tetragonal domains with spontaneous strain orientations both parallel and perpendicular to applied electric field (i.e., a and c oriented) appear in a narrow range of electric field magnitudes between 0.3 and 0.5 kV/mm. Figure 4(b) shows the relative volume fractions of cubic material as well as tetragonal domain variants with polarization parallel and perpendicularly to the electric field, as calculated from the integrated intensity of the 200/020/002 Bragg reflections. Importantly, the relative volume fraction changes indicate that, during the transformation, most of the diffracting volume in the sample is in either the cubic state or the tetragonal state polarized parallel to the electric field. The volume of material possessing the domain configuration polarized perpendicular to the electric field comprises only a small volume fraction of the total sample.

V. DISCUSSION

We postulate that the tetragonal domains polarized perpendicular to the electric field we observe in the x-ray diffraction measurements could be the same as those responsible for the square-net domain ordering seen in the polarized light microscopy. However, they are only observed in a narrow range of electric field magnitudes (0.3–0.5 kV/mm) compared

to our microscopy measurements (0.2 to > 1 kV/mm). One explanation for this difference is that it is a consequence of the fact that the x-ray measurements corresponded to a local spatial region of the sample determined by the beam size and diffracting volume ($200 \times 150 \times 1\ \mu\text{m}$), and was not representative of the entire square-net pattern observed by the microscope. Another explanation for this narrow region of stability is that the square-net pattern observed in the microscope might in fact *require* the temperature gradient induced by the silver electrode. This gradient was not present in the x-ray measurement, due the silver electrode covering the entire surface. We also note that, while the x-ray intensity measurements should accurately correlate the diffraction intensity to the volume fraction of material, the same cannot be said of the birefringence signal measured during the polarized light microscopy measurements, which only originates from the (potentially very small) birefringent regions of the material that are interacting with the polarized light.

All previous observations of these patterns have been conducted under zero external electric field [6–9], which means the net polarization of all possible domain configurations should also be zero. However, as we observe the same birefringence pattern under an external electric field, the domain structure is instead required to have a net polarization in response to the external field. In these previous observations without an external electric field, the organization of domains is related to the collapse of the tetragonality (c/a ratio) at T_C . For the electric field induced transition observed in this study we would, on the contrary, expect an increasing c/a ratio. From Fig. 4 we see that the tetragonal strain ($c/a - 1$) at the electric field induced transition (i.e., where the square-net birefringence pattern should be observed) is around 0.004—ten times larger than the “residual” strain measured in the zero field square-net patterns ~ 0.0003 [8].

The x-ray diffraction measurements showed that the relative volume fraction of parallel and perpendicularly polarized domain variants changes significantly under the application of electric fields, similar to where the square-net birefringence pattern is observed. To investigate how the domain variant fraction is manifest in the square-net pattern, we utilized the optical retardation model developed by [9]. We acknowledge that the slab model presented in the above is not mechanically compliant, but merely serves as a conceptual model showing the behavior of the system. As seen in Fig. 5(f) we simulate the square-net patterns behavior under increasing ratio of parallel to perpendicularly polarized domain widths within the birefringent slabs. At the ratio increases (presumably corresponding to an increase in applied electric field), we would assume that the domains polarized perpendicular to the electric field become narrower and the parallel wider. By calculating the birefringent behavior resulting from these changes in relative domain widths, we see a change in the aspect ratio of the (formerly) square features, along with a decreasing retardation, as shown in Figs. 5(a)–5(c). The changes observed in our polarized light microscopy measurements (e.g., Fig. 1) are, however, only small compared to simulated birefringent patterns shown in Figs. 5(d) and 5(e). From this we can conclude that the ratio of parallel to perpendicular polarized domains must be close to unity inside the slabs. As

FIG. 5. (a)–(c) Simulations of the birefringence patterns at parallel to perpendicular oriented domain width ratios of 1, 1.5, and 3. (d) and (e) Images of square-net pattern at 300 and at 800 V/m. We note that (d) and (e) are at the same position of the crystal. (f) Possible domain structure responsible for the square-net pattern. Blue regions are slab structures as described in [9]. White region corresponds to bulk domains with net polarization along the electric field direction.

the observed change in aspect ratio is so small, we conclude that the slabs are thin surface domains and that most of the sample volume is filled with domains polarized parallel to the electric field. In other words, this supports the commonly held belief that the square-net birefringence pattern, which requires domain polarizations parallel to the surface, is localized at the surface(s) of the crystal.

VI. CONCLUSIONS

In conclusion, we observed square-net birefringence patterns in BaTiO₃ single crystals grown by the top-seeded solution method. Uniquely, the square-net patterns were observed above T_C and under the application of electric fields with magnitudes of the order of 0.2 kV/mm. These observations contradict earlier assumptions that the pattern was restricted to flux-grown crystals below T_C . The square-net pattern appears to be stable over a wide range of temperatures and electric-field magnitudes, and in multiple samples. Furthermore, structural measurements obtained using high-energy synchrotron *in situ* x-ray diffraction support these findings. Collectively, these insights suggest that the formation of these spectacular square-net patterns may be more broadly occurring in BaTiO₃—and perhaps other ferroelectrics—than typically thought. To this end, we believe the investigation of the morphology of the domains within these square-net patterns using a nondestructive 3D mapping technique would shed considerable light on this long-standing conundrum.

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